Experimental investigation and thermodynamic modeling of the C-Me-O systems (where Me = Hf, Zr)

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Introduction

- Zirconium and hafnium carbide (ZrC_x and HfC_x) are considered as Ultra High Temperature Ceramics (UHTC) which can be easily oxidized under flowing dioxygen.
- Oxygen atoms can substitute carbon atoms in the crystalline lattice of carbides involving the formation of oxycarbide phases ZrC_xO_y and HfC_xO_y.
- The thermodynamic modeling of the C-Me-O ternary phase diagrams requires thermodynamic and diagrammatic data especially to determine the solubility of the oxygen into the carbide sublattice.

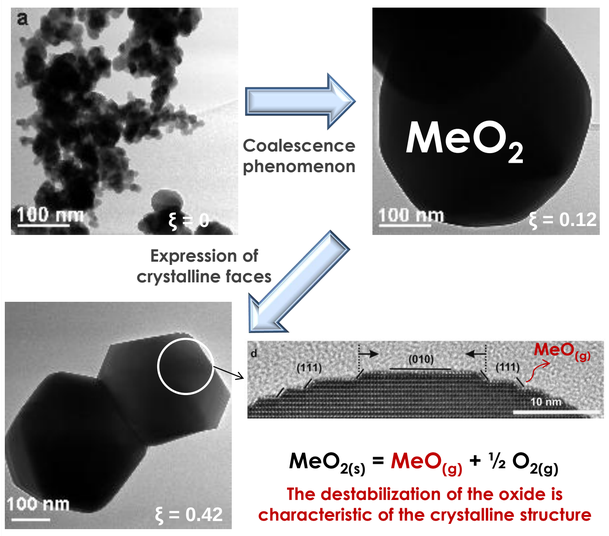
Experimental

Reaction mechanisms involved during the carbothermal reduction of ZrO_2 and HfO_2 [a, b]

$MeO_{2(s)} + 3\ C_{(s)} \rightarrow MeC_{(s)} + 2\ CO_{(g)}$

Structural approach by **XRD** and **TEM** → understanding of the reaction mechanisms involved for **different advancements ξ**.

Destabilization of ZrO_2 and HfO_2



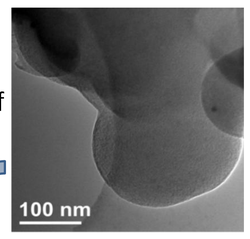
$MeO_{2(s)} = MeO_{(g)} + ½\ O_{2(g)}$

The destabilization of the oxide is characteristic of the crystalline structure

Destabilization of C

ξ = 0

Rounded carbon balls of 300 nm

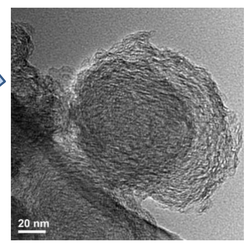


ξ > 0

Disruption of the external graphitic layers

Boudouard equilibrium

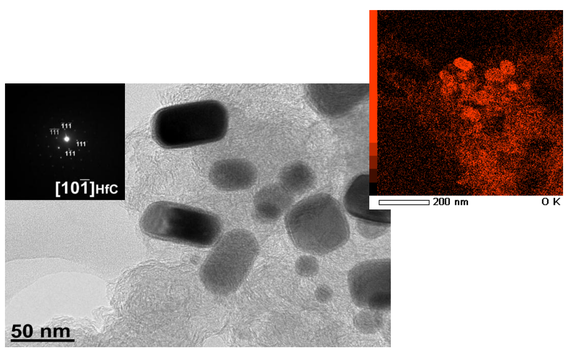
$C_{(s)} + CO_{2\,(g)} \rightarrow 2\ CO_{(g)}$



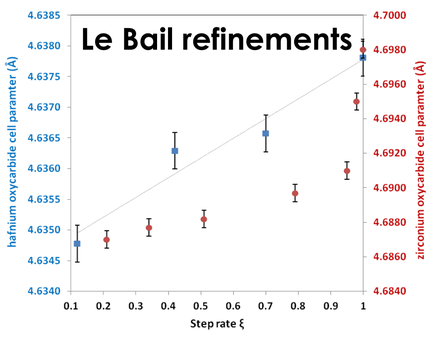
Nucleation of the MeC_xO_{1-x} phase

Co-condensation reaction of $MeO_{(g)}$ and $CO_{(g)}$ within carbon-rich areas

$MeO_{(g)} + 3x\ CO_{(g)} \rightarrow MeC_xO_{1-x(s)} + 2x\ CO_{2(g)}$



Evolution of the MeC_xO_{1-x} phase



The increase of the carbon amount in the crystalline structure implies the increase of the MeC_xO_{1-x} lattice parameter.

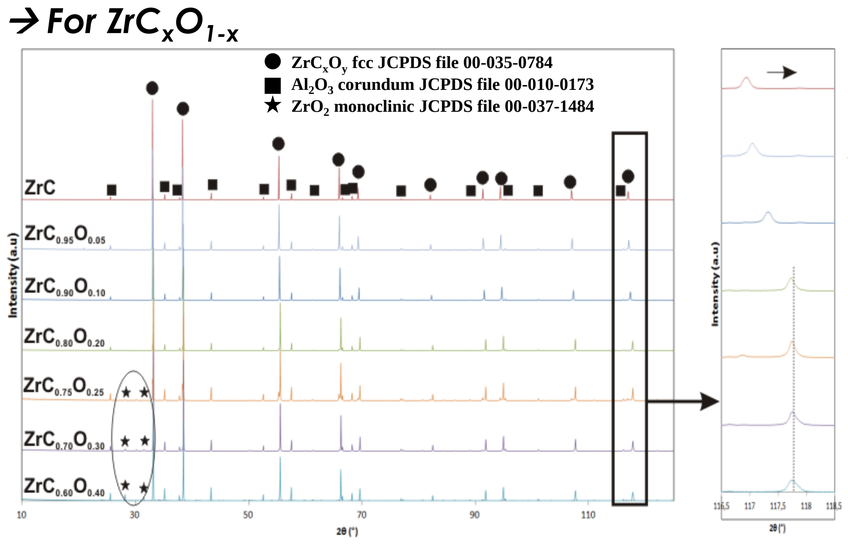
Purely reconstructive reaction → Impossible to obtain nanosized carbides by this synthesis way

Experimental determination of solid solution boundaries by carbothermal reduction

$MeO_{2(s)} + (1+2x)\ C_{(s)} \rightarrow MeC_xO_{(1-x)(s)} + (1+x)\ CO_{(g)}$

- The amount of initial reactants is adjusted to produce several oxycarbide stoichiometries.
- Heat treatment in a graphite furnace under flowing argon **at 1650°C, 1750°C and 1850°C** during 8 hours **(ξ = 1).**

→ ***For ZrC_xO_{1-x}***



The diffraction peaks of the zirconium oxycarbide shift towards high angles

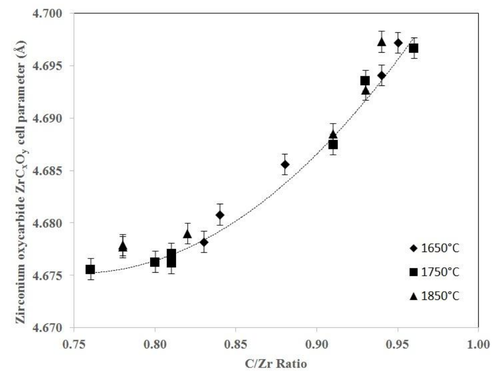
→ **Oxygen doping**

Stoichiometries in C and O of each sample computed by elemental analysis :

Temperatures	Low boundary	High boundary
1650°C	$ZrC_{0.83}O_{0.17}$	$ZrC_{0.94}O_{0.03}$
1750°C	$ZrC_{0.80}O_{0.20}$	$ZrC_{0.96}O_{0.04}$
1850°C	$ZrC_{0.78}O_{0.22}$	$ZrC_{0.94}O_{0.03}$

- **Increase of the maximum solubility of O with the increase of the temperature**
- **No modification of the maximum solubility of C with the temperature**

An abacus can be created correlating the lattice parameter and the stoichiometry of ZrC_xO_{1-x}

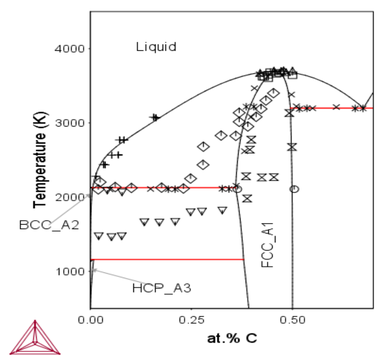


→ ***For HfC_xO_{1-x}***

- Between 1650°C and 1750 °C : no evolution of the solubility of O
- **At the same temperature, the stability domain of HfC_xO_{1-x} solid solution is narrower than ZrC_xO_y**

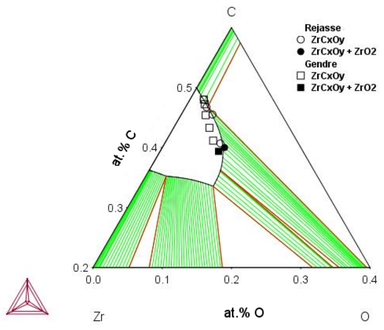
Thermodynamic Modeling

Binary diagram Zr-C [c]

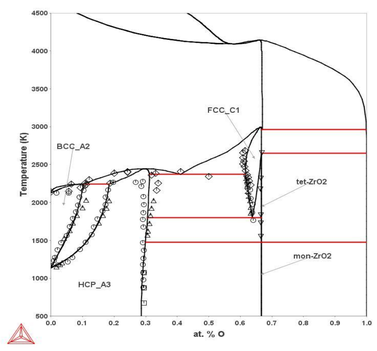


- FCC-A1 : $(Zr)_1(C,Va)_1$ / L^0, L^1
- C Graphite
- BCC_A2 : $(Zr)_1(C,Va)_3$ / L^0
- HCP_A3 : $(Zr)_1(C,Va)_{0.5}$ / L^0
- Liquid : $(Zr,C)_1$ / L^0, L^1, L^2

Extrapolation in the ternary system and result of optimisation



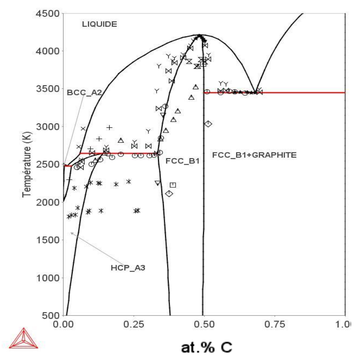
Binary diagram Zr-O [d]



- FCC-C1 : $(Zr)_1(O,Va)_2(O,Va)_1$/ L^0, L^1 , L^2
- BCC_A2 : $(Zr)_1(O,Va)_3$ / L^0
- HCP_A3 : $(Zr)_1(O,Va)_{0.5}$ / L^0
- Liquid : $(O,ZrO_2, Zr)_1$ / L^0, L^1, L^2

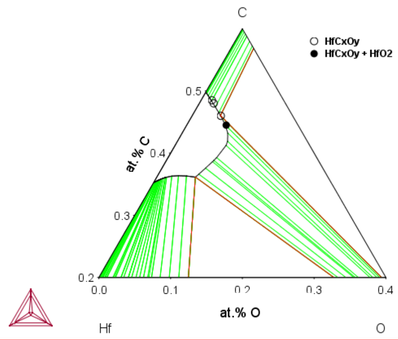
At 1750°C

Binary diagram Hf-C [e]

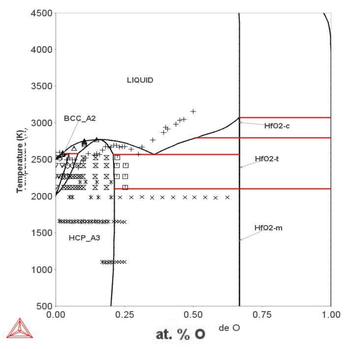


- FCC-B1 : $(Hf)_1(C,Va)_1$ / L^0, L^1
- C Graphite
- BCC_A2 : $(Hf)_1(C,Va)_3$ / L^0
- HCP_A3 : $(Hf)_1(C,Va)_{0.5}$/ L^0, L^1, L^2
- Liquid : $(Hf,C)_1$ / L^0, L^1, L^2, L^3

Extrapolation in the ternary system and result of optimisation



Binary diagram Hf-O [f]



- BCC_A2 : $(Hf)_1(O,VA)_3$ / L^0
- HCP_A3 : $(Hf)_1(O,Va)_{0.5}$ / L^0 , L^1
- Liquid : Ionic / L^0, L^1, L^2

At 1750°C

Summary

- The carbothermal reaction is a **purely reconstructive reaction** which operates through solid-gas equilibriums.
- This reaction allowed to determine the stability domains of MeC_xO_y solid solutions. On the Zr-C-O system, the extent of the domain increases with the temperature. At the same temperature, the domain of HfC_xO_y is narrower than ZrC_xO_y.
- These **experimental data** were used to assess the **two ternary phase diagrams** and to describe the evolution of the solid solutions with the temperature

a - J. David et *al.*, *J. Eur. Ceram. Soc.* **33** (2013) 165–179.
b - F. Réjasse et *al.*, J. David, *RSC Adv.* **5** (2015) 45341–45350.
c - A. Fernández Guillermet, *J. Alloys Compd.* **217** (1995) 69–89.
d - P.Y. Chevalier et *al.*, *Calphad*. **28** (2004) 15–40.
e - H. Bittermann, P. Rogl, *J. Phase Equilibria*. **18** (1997) 344–356.
f - D. Shin et *al.*, *Calphad*. **30** (2006) 375–386.

15th International IUPAC Conference on High Temperature Materials Chemistry HTMC XV, March 29 - April 1, 2016, Orléans - France